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(54) Title: THERMOPLASTIC VULCANIZATE COMPOSITION AND METHOD OF MAKING SAME

(57) Abstract: A thermoplastic vulcanizate composition comprises a mixture or reaction product of a branched thermoplastic polymer having a branching index of less than 1.0; a vulcanizable elastomer; and a cross-linking agent capable of vulcanizing the elastomer, wherein the cross-linking agent does not substantially degrade or cross-link the branched thermoplastic polymer. For example, a thermoplastic vulcanizate composition comprises a mixture or reaction product of a branched polypropylene having a branching index of less than 1.0; an EPDM elastomer having ethylenic unsaturation; and a phenolic resin, wherein the branched polypropylene has a molecular weight in the range from about 100,000 to 1,000,000 and has a melt strength which is at least about 50% higher than that of a linear polypropylene having the same molecular weight.

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## THERMOPLASTIC VULCANIZATE COMPOSITION AND METHOD OF MAKING SAME

### CROSS REFERENCE TO RELATED APPLICATIONS

Not applicable.

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### FEDERALLY SPONSORED RESEARCH STATEMENT

Not applicable.

### REFERENCE TO MICROFICHE APPENDIX

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Not applicable.

### FIELD OF THE INVENTION

This invention relates to thermoplastic vulcanizates with improved mechanical properties. The thermoplastic vulcanizate comprises a branched propylene polymer and an engineered thermoplastic elastomer.

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### BACKGROUND OF THE INVENTION

Elastomers are defined as materials which experience large reversible deformations under relatively low stress. Elastomers are typically characterized as having structural irregularities, non-polar structures, or flexible units in the polymer chain. Some examples of commercially available elastomers include natural rubber, ethylene/propylene (EPM) copolymers, ethylene/propylene/diene (EPDM) copolymers, styrene/butadiene copolymers, chlorinated polyethylene, and silicone rubber.

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Thermoplastic elastomers are elastomers having thermoplastic properties. That is, thermoplastic elastomers are optionally molded or otherwise shaped and reprocessed at temperatures above their melting or softening point. One example of thermoplastic elastomers is styrene-butadiene-styrene (SBS) block copolymer. SBS block copolymers exhibit a two phase morphology consisting of glassy polystyrene domains connected by rubbery butadiene segments.

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In contrast, thermoset elastomers are elastomers having thermoset properties. That is, thermoset elastomers irreversibly solidify or "set" when heated, generally due to an irreversible crosslinking reaction. A gel content of at least about 20 weight percent based on total elastomer as measured by xylene extraction is considered thermoset.

5 Two examples of thermoset elastomers are crosslinked ethylene-propylene monomer rubber (EPM) and crosslinked ethylene-propylene-diene monomer rubber (EPDM). EPM materials are made by copolymerization of ethylene and propylene. EPM materials are typically cured with peroxides to give rise to crosslinking, and thereby induce thermoset properties. EPDM materials are linear interpolymers of ethylene,  
10 propylene, and a nonconjugated diene such as 1,4-hexadiene, dicyclopentadiene, or ethylidene norbornene. EPDM materials are typically vulcanized with sulfur to induce thermoset properties, although they also can be cured with peroxides. While EPM and EPDM materials are advantageous in that they have applicability in higher temperature applications, EPM and EPDM elastomers have relatively low green strength (at lower  
15 ethylene contents), relatively low oil resistance, and relatively low resistance to surface modification.

Thermoplastic vulcanizates (TPV's) comprises thermoplastic matrices, preferably crystalline, through which thermoset elastomers are generally uniformly distributed. Examples of thermoplastic vulcanizates include ethylene-propylene monomer rubber  
20 and ethylene-propylene-diene monomer rubber thermoset materials distributed in a crystalline polypropylene matrix. One example of a commercial TPV is Satoprene® thermoplastic rubber which is manufactured by Advanced Elastomer Systems and is a mixture of crosslinked EPDM particles in a crystalline polypropylene matrix. These materials have found utility in many applications which previously used vulcanized  
25 rubber, e.g., hoses, gaskets, and the like.

Commercial TPVs are typically based on vulcanized rubbers in which a phenolic resin or sulfur cure system is used to vulcanize, that is to crosslink, a diene (or more generally, a polyene) copolymer rubber by way of dynamic vulcanization, that is crosslinking while mixing (typically vigorously), in a thermoplastic matrix.

30 Although numerous types of thermoplastic vulcanizates are known, there is still a need for improved thermoplastic materials having elastomeric properties. Specifically, there is a need for a method to produce thermoplastic vulcanizates having

improved tensile properties, elongation, compression set, and/or oil resistance. The improved properties would benefit not only current applications of thermoplastic vulcanizates but also new applications which require high melt strength, including blow molding, foams and wire cables.

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### SUMMARY OF THE INVENTION

Embodiments of the invention meet the above need by providing a thermoplastic vulcanizate composition which includes a mixture or reaction product of a branched thermoplastic polymer, a vulcanizable elastomer, and a cross-linking agent capable of vulcanizing the elastomer. The branched thermoplastic polymer has a branching index of less than 1.0. The cross-linking agent does not substantially degrade or cross-link the branched thermoplastic polymer. Various embodiments are described as follows.

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### BRIEF DESCRIPTION OF THE DRAWINGS

Not applicable.

### DESCRIPTION OF EMBODIMENTS OF THE INVENTION

Embodiments of the invention provide a thermoplastic vulcanizate (TPV) composition and a process for making various TPVs. For example, a thermoplastic vulcanizate composition comprises a mixture or reaction product of a branched thermoplastic polymer having a branching index of less than 1.0; a vulcanizable elastomer; and a cross-linking agent capable of vulcanizing the elastomer, wherein the cross-linking agent does not substantially degrade or cross-link the branched thermoplastic polymer. In some embodiments, a thermoplastic vulcanizate composition comprises a mixture or reaction product of a branched polypropylene having a branching index of less than 1.0; an EPDM elastomer having ethylenic unsaturation; and a phenolic resin, wherein the branched polypropylene has a weight-average molecular weight in the range from about 100,000 to 1,000,000 and has a melt strength which is at least about 50% higher than that of a linear polypropylene having the same weight-average molecular weight. In other embodiments, the TPVs do not

include or are substantially free of one or more plastomers. Such TPVs have lower compression set, higher tensile strength, elongation, and/or oil resistance.

### Definitions

5 In the following description, all numbers disclosed herein are approximate values, regardless whether the word "about" or "approximately" is used in connection therewith. They may vary by up to 1%, 2%, 5%, or sometimes 10 to 20%. Whenever a numerical range with a lower limit,  $R_L$ , and an upper limit  $R_U$ , is disclosed, any number  $R$  falling within the range is specifically disclosed. In particular, the following  
10 numbers  $R$  within the range are specifically disclosed:  $R = R_L + k \cdot (R_U - R_L)$ , wherein  $k$  is a variable ranging from 1% to 100% with a 1% increment, i.e.  $k$  is 1%, 2%, 3%, 4%, 5%, ..., 50%, 51%, 52%, ..., 95%, 96%, 97%, 98%, 99%, or 100%. Moreover, any numerical range defined by two numbers,  $R$ , as defined above is also specifically disclosed.

15 The term "thermoplastic vulcanizate" (TPV) refers to an engineering thermoplastic elastomer in which a cured elastomeric phase is dispersed in a thermoplastic matrix. It typically comprises at least one thermoplastic material and at least one cured (i.e., cross-linked) elastomeric material. Preferably, the thermoplastic material forms the continuous phase, and the cured elastomer forms the discrete phase;  
20 that is, domains of the cured elastomer are dispersed in the thermoplastic matrix. Preferably, the domains of the cured elastomer are fully and uniformly dispersed with the average domain size in the range from about 0.1 micron to about 100 micron, from about 1 micron to about 50 microns; from about 1 micron to about 25 microns; from about 1 micron to about 10 microns, or from about 1 micron to about 5 microns. In  
25 some embodiments, the matrix phase of the TPV is present by less than about 50% by volume of the TPV, and the dispersed phase is present by at least about 50% by volume of the TPV. In other words, the crosslinked elastomeric phase is the major phase in the TPV, whereas the thermoplastic polymer is the minor phase. TPVs with such phase composition have good compression set. However, TPVs with the major phase being  
30 the thermoplastic polymer and the minor phase being the cross-linked elastomer may also be made. Generally, the cured elastomer has a portion that is insoluble in cyclohexane at 23 °C. The amount of the insoluble portion is preferably more than

about 75% or about 85%. In some cases, the insoluble amount is more than about 90%, more than about 93%, more than about 95% or more than about 97% by weight of the total elastomer.

The branching index quantifies the degree of long chain branching in a selected thermoplastic polymer. Preferably, the branching index is less than about 0.9, 0.8, 0.7, 0.6 or 0.5. In some embodiments, the branching index is in the range from about 0.01 to about 0.4. In other embodiments, the branching index is less than about 0.01, less than about 0.001, less than about 0.0001, less than about 0.00001, or less than about 0.000001. It is defined by the following equation:

$$g' = \frac{IV_{Br}}{IV_{Lin}} \bigg|_{M_w}$$

where  $g'$  is the branching index,  $IV_{Br}$  is the intrinsic viscosity of the branched thermoplastic polymer (e.g., polypropylene) and  $IV_{Lin}$  is the intrinsic viscosity of the corresponding linear thermoplastic polymer having the same weight average molecular weight as the branched thermoplastic polymer and, in the case of copolymers and terpolymers, substantially the same relative molecular proportion or proportions of monomer units.

Intrinsic viscosity, also known as the limiting viscosity number, in its most general sense is a measure of the capacity of a polymer molecule to enhance the viscosity of a solution. This depends on both the size and the shape of the dissolved polymer molecule. Hence, in comparing a nonlinear polymer with a linear polymer of substantially the same weight average molecular weight, it is an indication of configuration of the nonlinear polymer molecule. Indeed, the above ratio of intrinsic viscosities is a measure of the degree of branching of the nonlinear polymer. A method for determining intrinsic viscosity of propylene polymer material is described by Elliott et al., J. App. Poly. Sci., 14, pp 2947-2963 (1970). In this specification the intrinsic viscosity in each instance is determined with the polymer dissolved in decahydronaphthalene at 135.degree. C. Another method for measuring the intrinsic viscosity of a polymer is ASTM D5225-98 - *Standard Test Method for Measuring Solution Viscosity of Polymers with a Differential Viscometer*, which is incorporated by reference herein in its entirety.

The term "plastomer" used herein refers to a copolymer of ethylene and an alpha-olefin comonomer wherein ethylene comprises from about 87 mole % to about 97.5 mole % of the plastomer copolymer; the alpha-olefin comonomer content comprises from about 13 to about 2.5 mole % of the plastomer copolymer and is incorporated into the copolymer in an amount that provides for a density of 0.92 g/cc or less and is limited in an amount so as not to reduce the density to a value less than 0.865 g/cc; and the distribution of the alpha-olefin comonomer within the copolymer is substantially random and also uniform among the differing molecular weight fractions that comprise the ethylene copolymer. This uniformity of comonomer distribution within the plastomer, when expressed as a comonomer distribution breadth index value (CDBI), provides for a CDBI greater than about 60, preferably greater than about 80 and more preferably greater than about 90. Further, the plastomer is characterized by a DSC melting point curve that exhibits the occurrence of a single melting point peak occurring in the region of 50 to 110 °C. (i.e., second melt rundown), and the plastomer has a molecular weight distribution ( $M_w/M_n$ ) value of less than about 4.0 and preferably less than about 3.5. Typically, the ethylene copolymer plastomer has a 1% secant modulus not exceeding about 15,000 and as low as about 800 psi or even less. Additional description of the plastomer can be found in column 8, line 11 to column 10, line 25 of U.S. Patent No. 6,207,754 B1. That portion of the specification is incorporated by reference herein.

The term "poly(sulfonyl azide)" used herein refers to any compound having at least two sulfonyl azide groups ( $--SO_2N_3$ ) reactive with a -C-H group, preferably a primary or secondary -C-H group, and/or an unsaturated group (such as a  $-C=C-$ ). Preferably, it is capable of reacting with a primary or secondary -C-H group of a polyolefin or an elastomer. The poly(sulfonyl azide) can be used as a coupling agent or a cross-linking agent in embodiments of the invention. Preferably the poly(sulfonyl azide)s have a structure  $X--R--X$  wherein each X is  $SO_2N_3$  and R represents an unsubstituted or inertly substituted hydrocarbyl, hydrocarbyl ether or silicon-containing group, preferably having sufficient carbon, oxygen or silicon, preferably carbon, atoms to separate the sulfonyl azide groups sufficiently to permit a facile reaction between the polyolefin and the sulfonyl azide, more preferably at least 1, more preferably at least 2, most preferably at least 3 carbon, oxygen or silicon, preferably carbon atoms between

functional groups. The term "inertly substituted" refers to substitution with atoms or groups which do not undesirably interfere with the desired reaction(s) or desired properties of the resulting crosslinked polymers. Such groups include fluorine, aliphatic or aromatic ether, siloxanes, as well as sulfonyl azide groups when more than two polyolefin chains are to be joined. Suitable structures include R as aryl, alkyl, aryl alkaryl, arylalkyl silane, or heterocyclic, groups and other groups which are inert and separate the sulfonyl azide groups as described. More preferably, R includes at least one aryl group between the sulfonyl groups, most preferably at least two aryl groups (such as when R is 4,4' diphenylether or 4,4'-biphenyl). When R is one aryl group, it is preferred that the group have more than one ring, as in the case of naphthylene bis(sulfonyl azides). Poly(sulfonyl)azides include such compounds as 1,5-pentane bis(sulfonylazide), 1,8-octane bis(sulfonyl azide), 1,10-decane bis(sulfonyl azide), 1,10-octadecane bis(sulfonyl azide), 1-octyl-2,4,6-benzene tris(sulfonyl azide), 4,4'-diphenyl ether bis(sulfonyl azide), 1,6-bis(4'-sulfonazidophenyl)hexane, 2,7-naphthalene bis(sulfonyl azide), and mixed sulfonyl azides of chlorinated aliphatic hydrocarbons containing an average of from 1 to 8 chlorine atoms and from about 2 to 5 sulfonyl azide groups per molecule, and mixtures thereof. Preferred poly(sulfonyl azide)s include oxy-bis(4-sulfonylazidobenzene), 2,7-naphthalene bis(sulfonyl azido), 4,4'-bis(sulfonyl azido)biphenyl, 4,4'-diphenyl ether bis(sulfonyl azide) and bis(4-sulfonyl azidophenyl)methane, and mixtures thereof.

### **Branched Thermoplastic polymers**

Any branched thermoplastic polymer with a branching index less than 1 can be used in embodiments of the invention so long as the resulting TPV has the desired physical properties. Suitable branched thermoplastic polymer include, but are not limited to, branched polyethylene (such as high density polyethylene), branched polypropylene, branched polycarbonate, branched polystyrene, branched polyethylene terephthalate, and branched nylon. Preferably, a branched thermoplastic polymer has a relatively high melt strength. Specifically, the melt strength of branched thermoplastic polymer is at least 25% higher than that of the corresponding linear thermoplastic polymer with the same weight average molecular weight. In some instances, the melt strength of a branched thermoplastic polymer is about 50% higher, about 75% higher,



about 100% higher, or about 150% higher than that of the corresponding linear thermoplastic polymer. In some embodiments, the melt strength of a branched thermoplastic polymer is at least about 10 cN, at least about 15 cN, at least about 20 cN, at least about 25 cN, at least about 30 cN, at least about 35 cN, or at least about 40 cN. In some embodiments, the 1% secant modulus of the branched thermoplastic polymer is equal to or higher than about 130,000 psi. It may also be higher than about 150,000 psi, higher than about 170,000 psi, or higher than about 200,000 psi.

A preferred thermoplastic polymer is branched polypropylene, both homopolymer and copolymer. One class of branched polypropylene is coupled impact propylene polymer. As used herein, "coupling" refers to modifying the rheology of a polymer by reacting the polymer with a suitable coupling agent. A "coupled polymer" is a rheology modified polymer resulting from a coupling reaction. A coupled polymer is characterized by an increase in melt strength of at least about 25% and a decrease in melt flow rate, compared to the polymer before coupling. A coupled polymer differs from a heavily crosslinked polymer in that the coupled polymer is thermoplastic and has a low gel level, i.e., a gel content of less than about 50% by weight, preferably less than about 30%, less than about 20%, less than about 10%, or less than about 5% by weight. In contrast, heavy crosslinking (otherwise known as "vulcanization") results in a thermoset polymer characterized by high gel levels, i.e., a gel content of more than about 50% by weight, preferably more than about 70%, more than about 80%, more than about 90%, or more than about 95% by weight.

One class of suitable coupled propylene polymers include those known as "Coupled Impact Polypropylene Polymers." Such polymers and their manufacture are disclosed in U.S. Patent No. 6,359,073, U.S. Patent Application Serial No. 09/017,230 filed on June 23, 2000 and in PCT Application No. WO 00/78858 A2, filed on June 23, 2000, which are incorporated by reference herein in their entirety. The process to produce a coupled impact propylene copolymer involves coupling of a impact propylene copolymer by a coupling agent. The coupling reaction is implemented via reactive extrusion or any other method which is capable of mixing the coupling agent with the impact propylene copolymer and adding sufficient energy to cause a coupling reaction between the coupling agent and the impact propylene copolymer. Preferably, the process is carried out in a single vessel such as a melt mixer or a polymer extruder,

such as described in U.S. Patent Application 09/133,576 filed August 13, 1998 which claims the benefit of U.S. Provisional Application No. 60/057,713 filed August 27, 1997, both of which are incorporated by reference herein in their entirety.

The term "impact propylene copolymer" is used herein to refer to heterophasic propylene copolymers where polypropylene is the continuous phase and an elastomeric phase is dispersed therein. Those of skill in the art recognize that this elastomeric phase may also contain crystalline regions, which for purposes of current embodiments of the invention are considered part of the elastomeric phase. The impact propylene copolymers result from an in-reactor process rather than physical blending. Usually the impact propylene copolymers are formed in a dual or multi-stage process, which optionally involves a single reactor with at least two process stages taking place therein, or optionally multiple reactors. Impact propylene copolymers are commercially available and are well known within the skill in the art, for instance, as described by E.P. Moore, Jr in Polypropylene Handbook, Hanser Publishers, 1996, page 220-221 and U.S. Patents 3,893,989 and 4,113,802, which are incorporated by reference herein in their entirety. Additional suitable impact propylene copolymers are disclosed in the following US patents: 4,434,264; 4,459,385; 4,489,195; 4,493,923; 4,508,872; 4,535,125; 4,588,775; 4,843,129; 4,966,944; 5,011,891; 5,034,449; 5,066,723; 5,177,147; 5,314,746; 5,336,721; 5,367,022; 6,207,754; 6,268,064, the pertinent part of the disclosure in each of the preceding patents is incorporated by reference therein.

A suitable coupling agent is a poly(sulfonyl azide), more preferably a bis(sulfonyl azide). Examples of poly(sulfonyl azides) useful in the thermoplastic vulcanizate are described in WO 99/10424. Poly(sulfonyl)azides include such compounds as 1, 5-pentane bis(sulfonyl azide), 1,8-octane bis(sulfonyl azide), 1,10-decane bis(sulfonyl azide), 1,10-octadecane bis(sulfonyl azide), 1-octyl-2,4,6-benzene tris(sulfonyl azide), 4,4'-diphenyl ether bis(sulfonyl azide), 1,6-bis(4'-sulfonazidophenyl)hexane, 2,7-naphthalene bis(sulfonyl azide), and mixed sulfonyl azides of chlorinated aliphatic hydrocarbons containing an average of from 1 to 8 chlorine atoms and from 2 to 5 sulfonyl azide groups per molecule, and mixtures thereof. Preferred poly(sulfonyl azide)s include oxy-bis(4-sulfonylazidobenzene), 2,7-naphthalene bis(sulfonyl azido), 4,4'-bis(sulfonyl azido)biphenyl, 4,4'-diphenyl ether bis(sulfonyl azide) and bis(4-sulfonyl azidophenyl)methane, and mixtures thereof.

Sulfonyl azides are commercially available or are conveniently prepared by the reaction of sodium azide with the corresponding sulfonyl chloride, although oxidation of sulfonyl hydrazines with various reagents (nitrous acid, dinitrogen tetroxide, nitrosonium tetrafluoroborate) has been used.

5        When a bis(sulfonyl azide) is used for the coupling agent, preferably at least about 100 ppm of azide is used for coupling the impact propylene copolymer, based on the total weight of the impact propylene copolymer, more preferably at least about 150 ppm of azide, most preferably at least about 200 ppm of azide is used. In some instances, such as where a large reduction in the ductile-to-brittle transition temperature  
10 is desirable as compared with the base comparable non-coupled impact propylene copolymer, at least about 300 ppm of bis(sulfonyl azide), preferably at least about 450 ppm of bis(sulfonyl azide) based on the total weight of the impact propylene copolymer is used for coupling the impact propylene copolymer. It is important in choosing the impact propylene copolymer to be coupled, that a polymer is chosen that has a high  
15 enough melt flow rate, so that after coupling with the desired amount of coupling agent, the coupled impact propylene copolymer has a sufficiently high melt flow rate to be readily processed.

In some embodiments, the coupled impact propylene copolymer is characterized by the following formula:

20

$$X = [(A-C)/(B-D)] \leq 0.75;$$

$$Y \geq 1.25; \text{ and}$$

$$A \leq B-10$$

25        where A is the ductile-to-brittle transition temperature calculated from notched Izod values (Measured in accordance with ASTM D-256) measured with the notch perpendicular to the polymer injection flow direction for an article made from the coupled impact propylene copolymer resin; B is the ductile-to-brittle transition temperature calculated from notched Izod values (Measured in accordance with ASTM  
30 D-256) measured with the notch perpendicular to the polymer injection flow direction for an article made from the corresponding non-coupled impact propylene copolymer resin; C is the ductile-to-brittle transition temperature calculated from notched Izod

values (Measured in accordance with ASTM D-256) measured with the notch parallel to the polymer injection flow direction for an article made from the coupled impact propylene copolymer resin; D is the ductile-to-brittle transition temperature calculated from notched Izod (Measured in accordance with ASTM D-256) measured with the notch parallel to the polymer injection flow direction for an article made from the corresponding non-coupled impact propylene copolymer resin.

Y is the ratio of the melt strength of the coupled impact propylene copolymer resin to the melt strength of the corresponding non-coupled impact propylene copolymer resin. In some embodiments, Y is at least about 1.5, at least about 2, at least about 5; or at least about 10. In other embodiments, X is less than about 0.5, less than about 0.33, or less than about 0.25.

The coupled impact propylene copolymer has improved impact properties when compared to those of a non-coupled impact propylene copolymer and also increases the melt strength of the resulting coupled impact propylene copolymer resin to a level of at least about 1.25 times, preferably at least about 1.5 times, that of a corresponding non-coupled impact propylene copolymer. The corresponding non-coupled impact propylene copolymer is the same polymer used to make the coupled impact propylene copolymer, but has not been coupled. Preferably, the coupled impact propylene copolymer resins have a melt strength of at least about 8, at least about 15 cN, at least about 30 cN, at least about 50 cN, or at least about 60 cN. In some embodiments, the melt flow rate of the coupled impact propylene polymer may range from about 0.01 to about 100 g/10 min., as measured according to ASTM 1238 at 230 °C. and 2.16 kg. Preferably, the melt flow rate is in the range from about 0.05 to about 50 g/10 min., about 0.1 to about 10 g/10 min., or about 0.5 to about 5 g/10 min.

Examples of impact properties that are improved in the coupled impact propylene copolymer compared to the corresponding non-coupled impact propylene copolymers include, for example, higher impact strength at low temperatures as exhibited by articles formed from the coupled impact propylene copolymer and an improvement in the ductile-to-brittle transition temperature, which is reduced in articles formed from the coupled impact propylene copolymer.

“Impact properties” refer to properties of articles such as impact strength, which is measured by any means within the skill in the art, for instance, Izod impact energy as

measured in accordance with ASTM D 256, MTS Peak Impact Energy (dart impact) as measured in accordance with ASTM D 3763-93, and MTS total Impact Energy as measured in accordance with ASTM D-3763. The ductile-to-brittle transition temperature (DBTT) is also an impact property of an article made from a polymer. The ductile-to-brittle transition temperature defines, for a given set of conditions, the temperature at which an object transitions from a predominantly ductile mode of failure to a predominantly brittle mode of failure. The ductile-to-brittle transition temperature can be calculated using techniques known to one of skill in the art.

Any amount of coupled impact propylene polymer may be used to make a TPV so long as the amount is sufficient for the coupled impact propylene polymer to be the thermoplastic matrix. Typically, the coupled impact propylene polymer is present in an amount of at least 10% by volume of the total TPV composition, preferably from about 15% to about 65%, from about 20% to about 50%, from 25% to about 45% or from about 30% to about 45%. Preferably, the coupled impact propylene polymer is the minor phase, i.e., it is present by less than 50% by volume of the TPV composition.

Examples of representative branched propylene polymers include Profax<sup>TM</sup> 814 and Profax<sup>TM</sup> 611 by Basell Polyolefins, the Netherlands or comparable polypropylene from The Dow Chemical Company, Midland, Michigan.

In addition to the branched propylene polymer described herein, suitable branched propylene polymers also include those disclosed in the following US patents: 4,311,628; 4,521,566; 4,916,198; 5,047,446; 5,047,485; 5,414,027; and 5,849,409 and in the following PCT patent applications: WO 01/53078; WO 97/20888; WO 97/20889; WO 99/10423; WO 99/10424; and WO 99/16797. All of the preceding patents or patent applications are incorporated by reference herein with respect to their disclosures of branched propylene polymers

### **Elastomers**

Any vulcanizable elastomer may be used to form a TPV, provided that it can be cross-linked (i.e., vulcanized) by a cross-linking agent. Vulcanizable elastomers, although thermoplastic in the uncured state, are normally classified as thermosets because they undergo an irreversible process of thermosetting to an unprocessable state. Preferably, the vulcanized elastomer is dispersed in a matrix of the thermoplastic

polymer as domains. The average domain size may range from about 0.1 micron to about 100 micron, from about 1 micron to about 50 microns; from about 1 micron to about 25 microns; from about 1 micron to about 10 microns, or from about 1 micron to about 5 microns.

5           One class of suitable elastomers includes, but is not limited to, an ethylene-higher alpha-olefin-polyene (EPDM) polymer. Any EPDM rubber which can be completely cured (cross-linked) with a phenolic curative or other cross-linking agent is satisfactory. Suitable monoolefin terpolymer rubber comprises essentially non-crystalline, rubbery terpolymer of two or more alpha monoolefins, preferably  
10 copolymerized with at least one polyene, usually a non-conjugated diene. Suitable EPDM rubbers comprise the products from the polymerization of monomers comprising two monoolefins, generally ethylene and propylene, and a lesser quantity of non-conjugated diene. The amount of non-conjugated diene is usually from about 2 to about 10 weight percent of the rubber. Any EPDM rubber which has sufficient  
15 reactivity with phenolic curative to completely cure is suitable. The reactivity of EPDM rubber varies depending upon both the amount of unsaturation and the type of unsaturation present in the polymer. For example, EPDM rubbers derived from ethylidene norbornene are more reactive toward phenolic curatives than EPDM rubbers derived from dicyclopentadiene and EPDM rubbers derived from 1,4-hexadiene are  
20 less reactive toward phenolic curatives than EPDM rubbers derived from dicyclopentadiene. However, the differences in reactivity can be overcome by polymerizing larger quantities of less active diene into the rubber molecule. For example, 2.5 weight percent of ethylidene norbornene or dicyclopentadiene may be sufficient to impart sufficient reactivity to the EPDM to make it completely curable  
25 with phenolic curative comprising conventional cure activators, whereas, at least 3.0 weight percent or more is required to obtain sufficient reactivity in an EPDM rubber derived from 1,4-hexadiene. Grades of EPDM rubbers suitable for embodiments of the invention are commercially available; Rubber World Blue Book 1975 Edition, Materials and Compounding Ingredients for Rubber, pages 406-410.

30           Generally, an EPDM elastomer has an ethylene content of from about 10% to about 90% by weight, a higher alpha-olefin content of about 10% to about 80% by weight, and a polyene content of about 0.5% to about 20% by weight, all weights based

on the total weight of the polymer. The higher alpha-olefin contains from about 3 to about 14 carbon atoms. Examples of these are propylene, isobutylene, 1-butene, 1-pentene, 1-octene, 2-ethyl-1-hexene, 1-dodecene, and the like. The polyene can be a conjugated diene such as isoprene, butadiene, chloroprene, and the like; a  
5 nonconjugated diene; a triene, or a higher enumerated polyene. Examples of trienes are 1,4,9-decatriene, 5,8-dimethyl-1,4,9-decatriene, 4,9-dimethyl-1,4,9-decatriene, and the like. The nonconjugated dienes are more preferred. The nonconjugated dienes contain from 5 to about 25 carbon atoms. Examples are nonconjugated diolefins such as 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene, 1,4-octadiene,  
10 and the like; cyclic dienes such as cyclopentadiene, cyclohexadiene, cyclooctadiene, dicyclopentadiene, and the like; vinyl cyclic enes such as 1-vinyl-1-cyclopentene, 1-vinyl-1-cyclohexene, and the like; alkylbicyclo nondienes such as 3-methyl-bicyclo (4,2,1) nona-3,7-diene, 3-ethylbicyclonondiene, and the like; indenenes such as methyl tetrahydroindene and the like; alkenyl norbornenes such as 5-ethylidene-2-norbornene,  
15 5-butyldiene-2-norbornene, 2-methyl-5-norbornene, 2-isopropenyl-5-norbornene, 5-(1,5-hexadienyl)-2-norbornene, 5-(3,7-octadienyl)-2-norbornene, and the like; and tricyclo dienes such as 3-methyl-tricyclo-(5,2,1,0<sup>sup</sup>.2,6)-3,8-decadiene and the like.

In some embodiments, the EPDM polymers contain from about 20% to about 80% by weight of ethylene, about 19% to about 70% by weight of a higher alpha-olefin, and about 1% to about 10% by weight of a nonconjugated diene. The more  
20 preferred higher alpha-olefins are propylene and 1-butene. The more preferred polyenes are ethylidene norbornene, 1,4-hexadiene, and dicyclopentadiene.

In other embodiments, the EPDM polymers have an ethylene content of from about 50% to about 70% by weight, a propylene content of from about 20% to about  
25 49% by weight, and a nonconjugated diene content from about 1% to about 10% by weight, all weights based upon the total weight of the polymer.

Examples of representative EPDM polymers for use include Nordel IP 4770R, Nordel 3722 IP available from DuPont Dow Elastomers, Wilmington, DE and Keltan 5636A available from DSM Elastomers Americas, Addis, LA.

30 The EPDM polymers, also known as elastomeric copolymers of ethylene, a higher-alpha-olefin and a polyene, have molecular weights from about 20,000 to about 2,000,000 or more. Their physical form varies from waxy materials to rubbers to hard

plastic-like polymers. They have dilute solution viscosities (DSV) from about 0.5 to about 10, measured at 30 °C on a solution of 0.1 gram of polymer in 100 cc of toluene.

Additional suitable elastomers are disclosed in the following U.S. patents:  
4,130,535; 4,111,897; 4,311,628; 4,594,390; 4,645,793; 4,808,643; 4,894,408;  
5 5,936,038, 5,985,970; and 6,277,916, all of which are incorporated by reference herein  
in their entirety.

### Cross-linking Agents

Any cross-linking agent which is capable of curing an elastomer without  
10 substantially degrading and/or curing the thermoplastic polymer used in a TPV can be  
used in embodiments of the invention. A preferred cross-linking agent is phenolic  
resin. Other curing agents include, but are not limited to, peroxides, azides, aldehyde-  
amine reaction products, substituted ureas, substituted guanidines; substituted  
xanthates; substituted dithiocarbamates; sulfur-containing compounds, such as  
15 thiazoles, imidazoles, sulfenamides, thiuramidisulfides, paraquinonedioxime,  
dibenzoparaquinonedioxime, sulfur; and combinations thereof. *See Encyclopedia of  
Chemical Technology*, Vol. 17, 2nd edition, Interscience Publishers, 1968; also  
*Organic Peroxides*, Daniel Seern, Vol. 1, Wiley-Interscience, 1970), which are  
incorporated by reference herein in their entirety.

20 Any phenolic curative system which can fully cure EPDM rubber is suitable.  
While it is preferred to fully cure the elastomer, it is not always necessary. In some  
embodiments, the elastomer is partially cured or substantially cured. A basic ingredient  
of such system is a phenolic curing resin made by condensation of halogen substituted  
phenol, C<sub>1</sub> -C<sub>10</sub> alkyl substituted phenol or unsubstituted phenol with an aldehyde,  
25 preferably, formaldehyde, in an alkaline medium or by condensation of bifunctional  
phenoldialcohols. Dimethylol phenols substituted in the para-position with C<sub>5</sub> -C<sub>10</sub>  
alkyl groups are preferred. Halogenated alkyl substituted phenol curing resins prepared  
by halogenation of alkyl substituted phenol curing resin are also especially suitable.  
Phenolic curative systems comprising methylol phenolic resins, halogen donor and  
30 metal compound are especially recommended, details of which are described in Giller,  
U.S. Pat. No. 3,287,440 and Gerstin et al, U.S. Pat. No. 3,709,840, which are  
incorporated by reference herein in their entirety. Another suitable class of phenolic



curative system is disclosed in U.S. Patent No. 5,952,42, which is incorporated by reference herein in its entirety. Non-halogenated phenol curing resins are used in conjunction with halogen donors, preferably, along with a hydrogen halide scavenger. Ordinarily, halogenated, preferably brominated, phenolic resins containing from about  
5 2 to about 10 weight percent bromine, do not require a halogen donor but are used in conjunction with a hydrogen halide scavenger such as metal oxides such as iron oxide, titanium oxide, magnesium oxide, magnesium silicate, silicon dioxide and preferably zinc oxide, the presence of which promotes the cross-linking function of the phenolic resin; however, with rubbers which do not readily cure with phenolic resins, the  
10 conjoint use of a halogen donor and zinc oxide is recommended. The preparation of halogenated phenol resins and their use in a curative system with zinc oxide are described in U.S. Pat. Nos. 2,972,600 and 3,093,613, the disclosures of which are incorporated herein by reference. Examples of suitable halogen donors are stannous chloride, ferric chloride, or halogen donating polymers such as chlorinated paraffin,  
15 chlorinated polyethylene, chlorosulfonated polyethylene, and polychlorobutadiene (neoprene rubber). The term "activator" as used herein means any material which materially increases the cross-linking efficiency of the phenolic curing resin and includes metal oxides and halogen donors either used alone or conjointly. For further details of phenolic curative systems see "Vulcanization and Vulcanizing Agents," W.  
20 Hoffman, Palmerton Publishing Company. Suitable phenolic curing resins and brominated phenolic curing resins are commercially available, for example, such resins may be purchased under the trade names SP-1045, CRJ-352, SP-1055 and SP-1056 from Schenectady Chemicals, Inc. Similar functionally equivalent phenolic curing resins may be obtained from other suppliers. As explained above, sufficient quantities  
25 of curatives are used to achieve essentially complete cure of the rubber.

Of course, it is understood that enough of phenolic curative is preferably used to fully cure the rubber. The minimum quantity of phenolic curative necessary to cure the rubber varies depending upon the type of rubber, phenolic curing agent, type of cure promoter and curing conditions such as temperature. Typically, the quantity of  
30 phenolic curing agent used to fully cure the EPDM rubber is from about 5 parts to about 20 parts by weight phenolic curing agent per 100 parts by weight of EPDM rubber. Preferably, the quantity of phenolic curing agent is from about 7 parts to about

14 parts by weight phenolic curing agent per 100 parts by weight EPDM rubber. In addition, an appropriate quantity of cure activator is used to assure full cure of the rubber. Satisfactory amounts of cure activator varies from about 0.01 parts by weight to about 10 parts by weight per 100 parts by weight EPDM rubber, although, higher  
5 amounts may be used, if desired and satisfactory cure is obtained. The term "phenolic curative" includes a phenolic curing agent (resin) and a cure activator. However, it should not be assumed, from the fact that the amount of phenolic curative is based on the EPDM rubber content of the blend that the phenolic curative does not react with the thermoplastic polymer resin or that there is no reaction between the thermoplastic  
10 polymer resin and EPDM rubber. There may be highly significant reactions involved but of limited extent, i.e., there is no substantial quantity of graft formation between the thermoplastic polymer resin and the EPDM rubber. Essentially all of the cured EPDM rubber and thermoplastic polymer resin can be separated and isolated from the blend by high temperature solvent extraction, for example, boiling xylene extraction and infrared  
15 analysis of the isolated fractions indicated that little, if any, graft copolymer is formed between the EPDM rubber and thermoplastic polymer resin.

In addition to phenolic curatives, azides may also be used as cross-linking agents. Suitable azides include, but are not limited to, azidoformates, such as tetramethylenebis(azidoformate) (see also U.S. Pat. No. 3,284,421, Breslow, Nov. 8,  
20 1966); aromatic polyazides, such as 4,4'-diphenylmethane diazide (see, also, U.S. Pat. No. 3,297,674, Breslow et al., Jan. 10, 1967); and sulfonazides, such as p,p'-oxybis(benzene sulfonyl azide).

A preferred class of azides is the poly(sulfonyl azide) described above. To crosslink, a poly(sulfonyl azide) is used in a crosslinking amount, that is an amount  
25 effective to crosslink the elastomer as compared with the starting material, that is sufficient poly(sulfonyl azide) to result in the formation of at least about 10 weight percent gels as evidenced by insolubility of the gels in boiling xylene when tested according to ASTM D-2765A-84. The amount is preferably at least about 0.5, more preferably at least about 1.0, most preferably 2.0 weight percent poly(sulfonyl azide)  
30 based on total weight of the elastomer, with these values depending on the molecular weight of the azide and the molecular weight or melt index of the elastomer. To avoid uncontrolled heating and unnecessary cost, degradation of physical properties, the

amount of poly(sulfonyl azide) is preferably less than about 10 weight percent, more preferably less than about 5.

Suitable peroxides as a cross-linking agent include, but are not limited to, aromatic diacyl peroxides; aliphatic diacyl peroxides; dibasic acid peroxides; ketone peroxides; alkyl peroxyesters; alkyl hydroperoxides (for example, diacetylperoxide; 5 dibenzoylperoxide; bis-2,4-dichlorobenzoyl peroxide; di-tert-butyl peroxide; dicumylperoxide; tert-butylperbenzoate; tert-butylcumylperoxide; 2,5-bis (t-butylperoxy)-2,5-dimethylhexane; 2,5-bis (t-butylperoxy)-2,5-dimethylhexyne-3; 4,4,4',4'-tetra-(t-butylperoxy)-2,2-dicyclohexylpropane; 1,4-bis-(t-butylperoxyisopropyl)-benzene; 1,1-bis-(t-butylperoxy)-3,3,5-trimethylcyclohexane; lauroyl peroxide; succinic acid peroxide; cyclohexanone peroxide; t-butyl peracetate; butyl hydroperoxide; etc.

#### Additives

15 The properties of a TPV may be modified, either before or after vulcanization, by addition of ingredients which are conventional in the compounding of EPDM rubber, thermoplastic polymer resin and blends thereof. Examples of such ingredients include particulate filler such as carbon black, silica, titanium dioxide, colored pigments, clay, zinc oxide and stearic acid, stabilizers, antidegradants, flame retardants, 20 processing aids, adhesives, tackifiers, plasticizers, wax, discontinuous fibers, such as wood cellulose fibers and extender oils. The addition of carbon black, extender oil or both, preferably prior to dynamic curing, are particularly recommended. Carbon black improves the tensile strength and tends to promote the phenolic curative. Extender oil can improve the resistance to oil swell, heat stability, hysteresis, cost and permanent set 25 of the elastoplastic composition. Aromatic, naphthenic and paraffinic extender oils are satisfactory. The addition of extender oil can also improve processability. For suitable extender oils, refer to Rubber World Blue Book, supra, pages 145-190. The quantity of extender oil added depends upon the properties desired, with the upper limit depending upon the compatibility of the particular oil and blend ingredients which limit is 30 exceeded when excessive exuding of extender oil occurs. Typically, from about 5 to about 300 parts by weight extender oil are added per 100 parts by weight blend of olefin rubber and thermoplastic polymer resin. Commonly, from about 30 to about 250

parts by weight of extender oil are added per 100 parts by weight of rubber present in the blend with quantities of from about 70 to about 200 parts by weight of extender oil per 100 parts by weight of rubber being preferred. The amount of extender oil depends, at least in part, upon the type of rubber. High viscosity rubbers are more highly oil extendable.

Colorable compositions are prepared by incorporation of non-black fillers instead of carbon black. Colorless, off-white or white pigments (fillers, extenders, or reinforcing pigments) such as silica, aluminum silicate, magnesium silicate, kaolin clay and titanium dioxide are suitable for such purposes. Preferably, a coupling agent such as titanates or silanes are used with non-black fillers especially with kaolin clay. Typically, from about 5 to about 100 parts by weight non-black pigment are added per 100 parts by weight of rubber in the blend. Typical additions of fillers either carbon black or non-black fillers comprise from about 40 to about 250 parts by weight of carbon black per 100 parts by weight of EPDM rubber and usually from about 10 to about 100 parts by weight filler per 100 parts total weight of EPDM rubber and extender oil. The amount of filler which can be used depends, at least in part, upon the type of filler and the amount of extender oil to be used.

#### **Method of Making TPVs**

Thermoplastic vulcanizates are typically prepared by blending plastic and cured rubbers by dynamic vulcanization. The compositions can be prepared by any suitable method for mixing of rubbery polymers including mixing on a rubber mill or in internal mixers such as a Banbury mixer. In the compounding procedure, the conventional compounding ingredients are incorporated. Such compounding ingredients may include one or more types of carbon black, additional extender oil, other fillers such as clay, silica, and the like, tackifiers, waxes, bonding resins and the like, zinc oxide, antioxidants, antiozonants, processing aids, and the cure active agents. Generally, it is preferred to add the cure active agents in a second stage of compounding which may be on a rubber mill or in an internal mixer operated at a temperature normally not in excess of about 60 °C. The cure active agents may include sulphur and the various sulphur containing accelerators. The compounds are cured in a conventional manner by heating for from about 5 to about 60 minutes at temperatures of from about 150 °C

to about 200 °C to form novel elastomeric vulcanizates having useful properties as described herein. Specific embodiments of the invention are hereinafter described, by way of illustration only.

Dynamic vulcanization is a process whereby a blend of plastic, rubber and rubber curative is masticated while curing the rubber. The term "dynamic" indicates the mixture is subjected to shear forces during the vulcanization step as contrasted with "static" vulcanization wherein the vulcanizable composition is immobile (in fixed relative space) during the vulcanization step. One advantage of dynamic vulcanization is that elastoplastic (thermoplastic elastomeric) compositions may be obtained when the blend contains the proper proportions of plastic and rubber. Examples of dynamic vulcanization are described in U.S. Pat. Nos. 3,037,954; 3,806,558; 4,104,210; 4,116,914; 4,130,535; 4,141,863; 4,141,878; 4,173,556; 4,207,404; 4,271,049; 4,287,324; 4,288,570; 4,299,931; 4,311,628 and 4,338,413 and are hereby incorporated by reference in their entirety.

Any mixer capable of generating a shear rate of 2000 sec<sup>-1</sup> or higher is suitable for carrying out the process. Generally, this requires a high speed internal mixer having a narrow clearance between the tips of the kneading elements and the wall. Shear rate is the velocity gradient in the space between the tip and the wall. Depending upon the clearance between the tip and the wall, rotation of the kneading elements from about 100 to about 500 revolutions per minute (rpm) is generally adequate to develop a sufficient shear rate. Depending upon the number of tips on a given kneading element and the rate of rotation, the number of times the composition is kneaded by each element is from about 1 to about 30 times per second, preferably from about 5 to about 30 times per second, and more preferably from about 10 to about 30 times per second. This means that material typically is kneaded from about 200 to about 1800 times during vulcanization. For example, in a typical process with a rotor with three tips rotating at about 400 rpm in a mixer having a residence time of about 30 seconds, the material is kneaded about 600 times.

A mixer satisfactory for carrying out the process is a high shear mixing extruder produced by Werner & Pfleiderer, Germany. The Werner & Pfleiderer (W&P) extruder is a twin-shaft screw extruder in which two intermeshing screws rotate in the same direction. Details of such extruders are described in U.S. Pat. Nos. 3,963,679 and

4,250,292; and German Pat. Nos. 2,302,546; 2,473,764 and 2,549,372, the disclosures of which are incorporated herein by reference. Screw diameters vary from about 53 mm to about 300 mm; barrel lengths vary but generally the maximum barrel length is the length necessary to maintain a length over diameter ratio of about 42. The shaft  
5 screws of these extruders normally are made-up of alternating series of conveying sections and kneading sections. The conveying sections cause material to move forward from each kneading section of the extruder. Typically there are about an equal number of conveying and kneading sections fairly evenly distributed along the length of the barrel. Kneading elements containing one, two, three or four tips are suitable,  
10 however, kneading elements from about 5 to about 30 mm wide having three tips are preferred. At recommended screw speeds of from about 100 to about 600 rpm and radial clearance of from about 0.1 to about 0.4 mm, these mixing extruders provide shear rates of at least from about 2000 sec<sup>-1</sup> to about 7500 sec<sup>-1</sup> or more. The net mixing power expended in the process including homogenization and dynamic  
15 vulcanization is usually from about 100 to about 500 watt hours per kilogram of product produced; with from about 300 to about 400 watt hours per kilogram being typical.

The process is illustrated by the use of W&P twin screw extruders, models ZSK-53 or ZSK-83. Unless specified otherwise, all of the plastic, rubber and other  
20 compounding ingredients except the cure activator are fed into the entry port of the extruder. In the first third of the extruder, the composition is masticated to melt the plastic and to form an essentially homogeneous blend. The cure activator (vulcanization accelerator) is added through another entry port located about one-third of the length of the barrel downstream from the initial entry port. The last two-thirds of  
25 the extruder (from the cure activator entry port to the outlet of the extruder) is regarded as the dynamic vulcanization zone. A vent operated under reduced pressure is located near the outlet to remove any volatile by-products. Sometimes, additional extender oil or plasticizer and colorants are added at another entry port located about the middle of the vulcanization zone.

30 The residence time within the vulcanization zone is the time a given quantity of material is within the aforesaid vulcanization zone. Since the extruders are typically operated under a starved condition, usually from about 60 to about 80 percent full,

residence time is essentially directly proportional to feed rate. Thus, residence time in the vulcanization zone is calculated by multiplying the total volume of the dynamic vulcanization zone times the fill factor divided by the volume flow rate. Shear rate is calculated by dividing the product of the circumference of the circle generated by the screw tip times the revolutions of the screw per second by the tip clearance. In other words, shear rate is the tip velocity divided by the tip clearance.

Methods other than the dynamic curing of rubber/thermoplastic polymer resin blends can be utilized to prepare compositions. For example, the rubber can be fully cured in the absence of the thermoplastic polymer resin, either dynamically or statically, powdered, and mixed with the thermoplastic polymer resin at a temperature above the melting or softening point of the resin. If the cross-linked rubber particles are small, well dispersed and in an appropriate concentration, the compositions are easily obtained by blending cross-linked rubber and thermoplastic polymer resin. It is preferred that a mixture comprising well dispersed small particles of cross-linked rubber is obtained. A mixture which contains poor dispersed or too large rubber particles can be comminuted by cold milling, to reduce particle size to below about 50  $\mu$ , preferably below about 20  $\mu$  and more preferably to below about 5  $\mu$ . After sufficient comminution or pulverization, a TPV composition is obtained. Frequently, poor dispersion or too large rubber particles is obvious to the naked eye and observable in a molded sheet. This is especially true in the absence of pigments and fillers. In such a case, pulverization and remolding gives a sheet in which aggregates of rubber particles or large particles are not obvious or are far less obvious to the naked eye and mechanical properties are greatly improved.

#### Applications of TPVs

Thermoplastic vulcanizate compositions are useful for making a variety of articles such as tires, hoses, belts, gaskets, moldings and molded parts. They are particularly useful for applications that require high melt strength such as large part blow molding, foams, and wire cables. They also are useful for modifying thermoplastic resins, in particular, thermoplastic polymer resins. The compositions can be blended with thermoplastic resins using conventional mixing equipment making a

rubber modified thermoplastic resin. The properties of the modified thermoplastic resin depend upon the amount of thermoplastic elastomer composition blended.

Additional TPV applications are disclosed in the following U.S. patents:  
6,329,463 entitled "High temperature, oil resistant thermoplastic vulcanizates made  
5 from polar plastics and acrylate or ethylene-acrylate elastomers;" 6,288,171 entitled  
"Modification of thermoplastic vulcanizates using random propylene copolymers;"  
6,277,916 entitled "Process for preparing thermoplastic vulcanizates;" 6,270,896  
entitled "Elastic fiber;" 6,235,166 entitled "Sealing means for electrically driven water  
purification units;" 6,221,451 entitled "Synthetic closure;" 6,207,752 entitled  
10 "Thermoplastic vulcanizates of carboxylated nitrile rubber and thermoplastic  
polyurethanes;" 6,174,962 entitled "Free radically cured thermoplastic vulcanizates of a  
polyolefin and a acrylate modified paraalkylstyrene/isoolefin copolymer;" 6,169,145  
entitled "Vulcanization of carboxyl containing elastomers using reductive  
hydrosilylation with extension into dynamic vulcanization;" 6,150,464 entitled  
15 "Preferred process for silicon hydride addition and preferred degree of polymerization  
for silicon hydride for thermoplastic vulcanizates;" 6,147,160 entitled "Organosilane  
cured butyl rubber/polypropylene TPV;" 6,100,334 entitled "Thermoplastic  
vulcanizates from a cyclic olefin rubber, a polyolefin, and a compatibilizer;" 6,084,031  
entitled "TPV from hydrosilylation crosslinking of acrylic modified bromo XP-50 butyl  
20 rubber;" 6,069,202 entitled "Thermoplastic elastomer triblend from an engineering  
thermoplastic, functionalized ethylene and or diene polymer, and brominated  
isobutylene p-methylstyrene copolymer;" 6,066,697 entitled "Thermoplastic  
compositions containing elastomers and fluorine containing thermoplastics;" 6,028,137  
entitled "Elastomeric compounds incorporating silicon-treated carbon blacks;"  
25 6,020,427 entitled "Thermoplastic vulcanizates of carboxylated nitrile rubber and  
polyester thermoplastics;" 5,977,271 entitled "Process for preparing thermoset  
interpolymers and foams;" 5,960,977 entitled "Corrugated polymeric filler neck  
tubing;" 5,957,164 entitled "Refrigerant hose;" 5,952,425 entitled "Preferred structure  
of phenolic resin curative for thermoplastic vulcanizate;" 5,939,464 entitled "High  
30 elasticity foams;" 5,936,038 entitled "Vulcanizable elastomeric composition and  
thermoplastic vulcanizate employing the same;" 5,869,591 entitled "Thermoset  
interpolymers and foams;" 5,750,625 entitled "Phenolic resin curatives which form



nonstaining thermoplastic elastomers;" 5,744,238 entitled "Dimensionally stable sheet handling shaft assembly and method of making same;" 5,621,045 entitled "Thermoplastic vulcanizates from isobutylene rubber and either EPDM or a conjugated diene rubber;" and 4,783,579 entitled "Flat multi-conductor power cable with two  
5 insulating layers." All of the preceding patents are incorporated by reference in their entirety herein.

### EXAMPLES

The following examples are given to illustrate various embodiments of the  
10 invention. They do not intend to limit the invention as otherwise described and claimed herein. All numerical values are approximate. When a numerical range is given, it should be understood that embodiments outside the range are still within the scope of the invention unless otherwise indicated. In the following examples, various polymers were characterized by a number of methods. Performance data of these polymers were  
15 also obtained. Most of the methods or tests were performed in accordance with an ASTM standard, if applicable, or known procedures.

Various formulations were weighed and mixed in the following manner, using an electrically heated Brabender batch mixer equipped with sigma blades at about 75 rpm and about 185 °C. Components for each batch were weighed in four groups: (1)  
20 elastomer, polypropylene, stabilizer, and processing aid; (2) oil; (3) curing agent; and (4) zinc oxide.

Three types of EPDM elastomer designated as "EPDM1," "EPDM2," and "EPDM3" were used. Representative components of the batch are shown below with their accompanying properties. The elastomer that is representative of EPDM1 include  
25 Keltan<sup>TM</sup> 5636A by DSM Copolymer Inc., Addis, LA, which is a copolymer of ethylene, propylene, and ethylidene norbornene (ENB) and has the following properties.

Property	Value	Test Method
Mooney Viscosity ML 1 + 4 at 125°C	50 - 60	ASTM D-1646
Composition, Ethylene, wt% ENB, wt%	68 - 72 4 - 5	ASTM D-3900
Specific Gravity	0.86	
Melt Flow, 10 kg @ 230 °C., dg/min.	2.7	ASTM D 1238

The elastomer that is representative of EPDM2 include Nordel™ 4770 by DuPont Dow Elastomers, Wilmington, DE, and has the following properties.

Property	Value	Test Method
Mooney Viscosity ML 1 + 4 at 125°C	70	ASTM D-1646
Composition, Ethylene, wt% Propylene, wt% ENB, wt%	70 25 5	ASTM D-3900 ASTM D-3900 ASTM D-6047
Molecular Weight Distribution	Medium	DuPont Dow PQ-E-034 and 036
Specific Gravity	0.87	ASTM D-297
Residual Transition Metal, ppm	< 10	DuPont Dow
Ash Content, wt%	<0.1	ASTM D-5667
Total Volatiles, wt%	<0.4	DuPont Dow PQ-E-007

The elastomer that is representative of EPDM3 include Nordel™ 3722IP by DuPont Dow Elastomers, Wilmington, DE, and has the following properties.

Property	Value	Test Method
Mooney Viscosity ML 1 + 4 at 125°C	20	ASTM D-1646
Composition, Ethylene, wt%	70.5	ASTM D-3900
Propylene, wt%	29	ASTM D-3900
ENB, wt%	0.5	ASTM D-6047
Molecular Weight Distribution	Medium	DuPont Dow PQ-E-034 and 036
Specific Gravity	0.88	ASTM D-297
Residual Transition Metal, ppm	< 10	DuPont Dow
Ash Content, wt%	<0.1	ASTM D-5667
Total Volatiles, wt%	<0.4	DuPont Dow PQ-E-007

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Four kinds of polypropylene were used: PP1, PP2, PP3, and PP4. The polypropylene that is representative of PP1 is a coupled impact propylene copolymer and typically has properties as follows. It has a branching index of less than 1.

Property	Value	Test Method
<b>Resin Properties</b>		
Melt Flow Rate (230 °C, 2.16 kg), g/10 min	0.4	ASTM D-1238
Density, g/cc	0.9	ASTM D-792
DSC Melting Point, °C	164	Dow Method
Melt Strength, cN (230 °C)	>10	Dow Method
<b>Film Properties, 50</b>		
Puncture Resistance, J/cm <sup>3</sup>	10.5	Dow Method
Dart Impact (Method A), g	150	ASTM D-1709
Tensile Yield, MPa		
MD	31	ASTM D-882
CD	26	
Ultimate Tensile, MPa		
MD	50	ASTM D-882
CD	42	
Ultimate Elongation, %		
MD	560	ASTM D-882
CD	750	
Tensile Modulus, 2% Secant, MPa		
MD	915	ASTM D-882
CD	792	

5

PP1 can be made according to the following procedures.

#### Base Polypropylene Resin

The base polypropylene used to make PP1 used in the following examples is isotactic polypropylene pellets, available from The Dow Chemical Company under the designation DC111. DC111 is an impact copolymer of propylene with 7-9 weight

percent of ethylene, melt flow rate (MFR) = 0.68 g/10 min and melt strength of approximately 12 cN.

#### Preparation of DPO-BSA Coupling Agent

5        4,4'-Oxydibenzenesulfonyl azide (hereinafter in the examples referred to as "DPO-BSA" or the "DPO-BSA coupling agent") used to make PP1 is prepared by the reaction of sodium azide with the corresponding bis(sulfonyl chloride) which is commercially available. An aqueous solution of sodium azide is added to an acetone solution of the bis(sulfonyl chloride), and the product is isolated by precipitation with  
10        excess water.

#### Preparation of DPO-BSA Concentrate Master Batch

52.25 lb/hr (23.75 Kg/hr) of AFFINITY™ EG-8200, (1-octene based polyethylene plastomer having a 5 g/10 min MI, and a 0.87 g/cc density, commercially  
15        available from the Dow Chemical Company) and 2.75 lb/hr (1.25 Kg/hr) of DPO-BSA are separately fed into a 30 mm twin screw extruder manufactured by Werner & Pfleiderer, model # ZSK-30. The extruder has an inlet/feed throat and additional 5 zones following the inlet. The temperature profile for the extruder is shown below. These temperatures, except for the Melt Temperature, are barrel temperatures for the  
20        extruder. The resulting melt-extruded mixture of EG-8200 and DPO-BSA is passed through a strand die located at the exit of zone #5 and then through a cooling water bath (water temperature 20 C) before being pelletized. The resulting DPO-BSA Concentrate Master Batch contains 5 weight percent DPO-BSA.

#### Preparation of PP1

25        PP1 is produced as follows. 1547 lb/hr (703.2 Kg/hr) of DC111 is fed into a 92 mm twin screw extruder manufactured by Werner & Pfleiderer, model # ZSK-92, using an individual feeder inlet.

30        The DPO-BSA Concentrate Master Batch and additional DC111 are first fed into a blender with a weight ratio of 95.93 to 4.07 of DC 111 to DPO-BSA Concentrate Master Batch to insure homogeneous mixing. The above mixture is then fed into the same 92 mm twin screw extruder as the DC111 via another individual feeder inlet at a

rate of 123 lb/hr ( 55.9 Kg/hr). The feed rate of the DC 111/DPO-BSA Concentrate is adjusted to introduce about 150 ppm of DPO-BSA based on the total weight of the polymers present. An additive package is added via a third feeder. The additive package includes a phenolic stabilizer available from Ciba Specialty Chemicals Company under the trade name IRGANOX 1010, a phosphite stabilizer available from Ciba Specialty Chemicals Company under the trade name IRGAFOS 168, calcium stearate, and glycerol monostearate. The feed rate of the additives is adjusted so that the resulting modified polymer resin has approximately 0.05 wt% of Calcium Stearate, approximately 0.06 wt% IRGANOX 1010, approximately 0.04 wt% IRGAFOS 168 and approximately 0.04 wt% glycerol monostearate.

The feed throat of the extruder is purged with nitrogen to reduce the oxygen level in the extruder. The temperature profile across the twin screw extruder from inlet to outlet is 200, 195, 180, 245, 245, 240, 240, 242, 242, and 253 C. The temperatures listed are barrel temperatures in the extruder. A die located at the outlet of the last zone should have a temperature of 250-270 C to ensure the full reaction of the BSA and propylene polymer. The resulting melt-extruded polymer is passed through the die and then pelletized. The resulting coupled resin material is PP1 (0.35 MFR, 0.900 g/cc density, melt strength 71 cN, and approximately 7-9 weight percent ethylene content).

Melt Strength (MS) is measured by using a capillary rheometer fitted with a 2.1 mm diameter, 20:1 die with an entrance angle of approximately 45 degrees. After equilibrating the samples at 190°C for 10 minutes, the piston is run at a speed of 1 inch/minute (2.54 cm/minute). The standard test temperature is 190°C. The sample is drawn uniaxially to a set of accelerating nips located 100 mm below the die with an acceleration of 2.4 mm/sec<sup>2</sup>. The required tensile force is recorded as a function of the take-up speed of the nip rolls. The maximum tensile force attained during the test is defined as the melt strength. In the case of polymer melt exhibiting draw resonance, the tensile force before the onset of draw resonance was taken as melt strength. The melt strength is recorded in centiNewtons ("cN")

A linear polypropylene designated as PP2 is an impact propylene copolymer. A representative PP2 is the Dow 104-01 polypropylene resin available from The Dow Chemical Company, Midland, MI, and has properties as follows. It is a linear polymer and thus has a branching index of 1.

5

Property	Value	Test Method
<b>Resin Properties</b>		
Melt Flow Rate (230 °C, 2.16 kg), g/10 min	1.2	ASTM D-1238
Density, g/cc	0.9	ASTM D-792
<b>Molded Part Properties</b>		
Tensile Strength at Yield, MPa	27.5	ASTM D-638
Tensile Elongation at Yield, %	10.0	ASTM D-638
Flexural Modulus, MPa	1240	ASTM D-970
Notched Izod Impact @ 23 °C, J/m	160.0	ASTM D-256A
Deflection Temperature Under Load @ 0.45 MPa, unannealed, °C	90	ASTM D-648

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The polypropylene that is representative of PP3 include branched propylene homopolymer such as Profax™ 814 by Basell Polymers, The Netherlands, and has properties as follows. It has a branching index of less than 1.

Property	Value	Test Method
<b>Physical</b>		
Density (Method B)	0.902	ASTM D-792
Melt Flow Rate (230 °C, 2.16 kg), g/10 min	3.0	ASTM D-1238
Water Absorption @ 24 hours, %	0.03	ASTM D-570
Water Absorption @ Saturation, %	0.2	ASTM D-570
<b>Mechanical</b>		
Tensile Strength @ Yield, MPa	35.8	ASTM D-638
Tensile Elongation @ Yield, %	9.0	ASTM D-638
Flexural Modulus, 1% Secant, MPa	1447	ASTM D-638
<b>Impact</b>		
Notched Izod Impact @ 23 °C, J/m	48	ASTM D-256
<b>Thermal</b>		
DTUL @ 6,8 kPa – Unannealed, °C	110	ASTM D-648
Max. Continuous Use Temp, °C	104	ASTM D-794
Melting Point, °C	167	

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The polypropylene that is representative of PP4 include an propylene polymer such as Profax™ 6523 by Basell Polymers, The Netherlands, and has properties as follows. It is a linear polymer and thus has a branching index of 1.

Property	Value	Test Method
<b>Physical</b>		
Density (Method B)	0.900	ASTM D-792
Melt Flow Rate (230 °C, 2.16 kg), g/10 min	4.0	ASTM D-1238
Water Absorption @ 24 hours, %	0.03	ASTM D-570
Water Absorption @ Saturation, %	0.2	ASTM D-570
<b>Mechanical</b>		
Tensile Strength @ Yield, MPa	33.7	ASTM D-638
Tensile Elongation @ Yield, %	12.0	ASTM D-638
Flexural Modulus, 1% Secant, MPa	1378	ASTM D-638
<b>Impact</b>		
Notched Izod Impact @ 23 °C, J/m	37.3	ASTM D-256
<b>Thermal</b>		
DTUL @ 6.8 kPa – Unannealed, °C	93	ASTM D-648
Max. Continuous Use Tmp, °C	104	ASTM D-794
Melting Point, °C	167	

- 5           The cross-linking agent was a phenolic curing agent available as SP1055 from Schenectady Chemicals, Schenectady, NY. Additives also included zinc oxide available as Kadox 911 from Zinc Corporation of America, Monaca, PA; a mineral paraffinic process oil available as Lyon Tuflo 6056 from Tulcom Oil, Inc., Arlington, Texas, a black color concentrate available as SPD black from M. A. Hanna; zinc
- 10   stearate (0.5%) as processing aid from Harwick Chemicals located in Ohio; an antioxidant blend (1:1 blend of Irganox 1076 and Irgafos 168 from Ciba Specialty Chemicals, Basel, Switzerland)

Sixteen formulations were blended having the compositions shown in Tables 1 and 2. Examples with the letter C prefix are comparative examples.

Table 1: Formulations for making TPV

Component (phr)	E 1	E 2	E 3	E 4	E 5	E 6	C 5	C 6	C 7	C 8
PP1*	44.81	61.15	85.28	123.13	38.94	54.10	0.00	0.00	0.00	0.00
PP2	0.00	0.00	0.00	0.00	0.0	0.0	38.32	54.48	92.48	133.66
EPDM1	0.00	0.00	85.28	61.57	118.01	108.20	116.13	108.95	0.00	0.00
EPDM2	101.84	91.72	0.00	0.00	0.0	0.0	0.00	0.00	69.36	50.12
EPDM3	33.95	30.57	0.00	0.00	0.0	0.0	0.00	0.00	23.12	16.71
Curing agent	6.79	8.56	7.68	7.39	8.26	7.57	8.13	5.45	11.10	6.01
ZnO	3.39	2.14	3.84	1.85	2.07	1.89	4.06	1.36	5.55	1.50
Plasticizer	33.95	30.57	42.64	30.78	59.01	54.10	58.07	54.48	23.12	16.71
SPD black	2.00	2.00	2.00	2.00	1.74	1.77	2.00	2.00	2.00	2.00
Processing aid	2.25	2.25	2.25	2.25	1.95	1.99	2.25	2.25	2.25	2.25
Stabilizer	0.56	0.56	0.56	0.56	0.49	0.5	0.56	0.56	0.56	0.56
Simpac 710	22.47	22.47	22.47	22.47	19.53	19.88	22.47	22.47	22.47	22.47
Total	252.00	252.00	252.00	252.00	250	250.00	252.00	252.00	252.00	252.00

\* indicates branched propylene polymer.

Table 2: Formulation of TPV

Formulation (phr)	E 9	E 10	E 11	E 12	E 13	E 14	C 15	C 16
PP1*	27.54	38.35	63.08	97.60	0.0	0.0	0.00	0.00
PP2	0.00	0.00	0.00	0.00	0.0		0.00	0.00
PP3*	83.46	76.70	63.08	48.80	86.73	125.1 3	0.00	0.00
PP4	0.00	0.00	0.00	0.00	0.0	0.0	96.14	135.1 7
EPDM1	0.00	0.00	63.08	48.80	86.73	62.57	0.00	0.00
EPDM2	62.60	57.52	0.00	0.00	0.0	0	72.10	50.69
EPDM3	20.87	19.17	0.00	0.00	0.0	0	24.03	16.90
Curing agent	7.51	9.20	3.15	3.42	6.07	4.38	6.73	3.38
ZnO	1.88	4.60	0.79	1.71	1.52	1.09	1.68	1.69
Plasticizer	20.87	19.17	31.54	24.40	43.37	31.28	24.03	16.90
SPD black	2.00	2.00	2.00	2.00	1.88	1.87	2.00	2.00
Processing aid	2.25	2.25	2.25	2.25	2.11	2.10	2.25	2.25
Stabilizer	0.56	0.56	0.56	0.56	0.53	0.53	0.56	0.56
Simpac 710	22.47	22.47	22.47	22.47	21.08	21.04	22.47	22.47
Total	252.0 0	252.0 0	252.0 0	252.0 0	250	250	252.0 0	252.0 0

\* indicates branched propylene polymer.

5 The mixing process was as follows:

- (1) Charge mixture comprising EPDM, PP, Stabilizer and Processing aid;
- (2) Mix to form homogeneous melt (approximately 2 minutes);
- (3) Add phenolic resin (approximately 190 °C) and lower the ram;

- (4) Add all of the oil "on top of the ram" – allowing only small amount of oil to enter in the chamber each time ram makes up ward movement. (do not oil directly into chamber);
- (5) After torque begins to increase (at about 195 °C or about three minutes after all oil is incorporated), add zinc oxide and continue to mix for about two minutes;
- (6) Remove mass from Brabender by "reverse jogging". If material is well mixed, it does not stick to chambers and comes out fairly easily. If material is "scorched" or "pre-cured" it sticks to rotors and does not come out easily;
- (7) Cool melt and granulate;
- (8) Compression mold 6"x6"x0.125" plaques at about 185 °C for about three minutes and cool using forced air;
- (9) Extrude 4"x0.050" thick ribbons using ¾", 3:1 L/D extruder with zone temperatures about 390 °F/ about 390 °F/ about 390 °F/ and die at about 430 °F.;
- (10) Die cut samples from compression molded and extruded ribbons using appropriate die;
- (11) Condition samples at room temperature for about 24 hours.

#### TESTING

- The following tests were performed on the examples and the results can be found in Tables 3 and 4.

- (1) Specific gravity according to ASTM D 792.
- (2) Tensile strength and elongation at break according to ASTM D 412 (2" jaw separation, 20 ipm crosshead speed, and 23 °C/50% RH).
- (3) Stress at 100%, 200%, and 300% elongation according to ASTM D 412 (2" jaw separation, 20 ipm crosshead speed, and 23 °C/50% RH).
- (4) Compression set (ASTM 395 Method B), 70 °C for 22 hours.
- (5) Hardness according to ASTM D 2240 (hand-held Durometer Shore A and Shore D, report readings after 5 second delay, i.e., relaxed).
- (6) Weight gain in ASTM # 3 oil (70 °C, 23 °C, 24 hours).

(7) Percent of crosslinked rubber via Extraction in boiling Xylene in accordance with ASTM D 2765-84.

Melt Flow Rate (MFR) according to ASTM D 1238 at 230 °C., 10 kg or 15 kg weights, 5 minute peaheat.

5

Table 3: Properties of TPV

Experiment #	E 1	E 2	E 3	E 4	E 5	E 6	C 5	C 6	C 7	C 8
Specific Gravity	0.943	0.953	0.954	0.95			0.949	0.938	0.969	0.947
Texture	2	2	3	4	Good	Good	Good	2	2	3
Hardness A, 10 sec	76	85	88	98	65*	72*	68	76	92	97
Hardness D, 10 sec	18	23	27	40			15	18	36	45
MFR (230C, 15)	0.458	0.908	4.92	13.7	0.26	1.14	0.62	5.25	3.83	21.54
MFR (230, 10)	0.21	0.37	0.81	4.6	0.05	0.23	0.17	2.05	1.46	6.54
Ratio	2.18	2.45	6.07	2.98	5.2	4.96	3.65	2.56	2.62	3.29
Tensile, Str, psi*	710	691	865	1425			742	520	1348	1180
100% stress	487	694	784	1318			386	424	1213	1150
200% stress	544						527	518	1293	1110
% elongation @ break	250	104	148	164			370	195	163	180
Tensile Str, psi**	920	1137	1352	1853	1018	1026	742	781	1478	1717
100% stress	518	689	822	1317	453	555	386	590	1006	1175
200% stress	683	885	1032	1503	669	770	527	712	1242	1437
300% stress	851	1114	1228	1743	323	321	632			1673
% elongation @ break	320	312	336	330			370	243	283	291
Compression Set%										
23 C, 22 hours	17	31	26	39	7.2	14	21.5	24	34	42
70 C, 22 hours	49	32.8	39	49	13	31	38.6	58.26	51.3	67.22
Oil Swell %w/w										
23 C, 22 hrs	46	33	25	15	27.7	17.96	41	46	24	21
70 C, 22 hrs	88	56	44	36	88	90	102	74	40	29
% gel, Xylene	60.05	78.61	85.18	101			81.5	64.06	83.91	92.06

\* Measured on compressed molded part

\*\* Measured on extruded part

5

Table 4: Properties of TPV

Experiment #	E 9	E 10	E 11	E 12	E 13	E 14	C 15	C 16
Sp. Gr	0.957	0.972	0.956	0.957			0.943	0.938
Texture	2	3	4	4			3	4
Hardness A, 10sec	73	86	94	98	87*	96*	96	98
Hardness D, 10sec	21	25	40	45			40	52
MFR (230C, 15)	0.624	0.667	22.87	81.59	1.17	17.7	11.52	68.97
MFR (230, 10)	0.051	0.105	8.72	26.4	0.26	5.2	3.18	6.12
Ratio	12.24	6.36	2.62	3.09	4.5	3.4	3.62	11.27
Tensile Str, psi	1166	1395	1275	1457			1450	
100% stress	583	853	1085	1462			1294	
200% stress	792	1084	1263					
% elongation @ break	336	300	212	88			158	
Tensile Str, psi	1166	1395	2043	2300	1605	2600	1559	1962
100% stress	583	853	1439	1526	889	1509	1116	1808
200% stress	792	1084	1671	1714	1122	1700	1364	1289
300% stress			1322	2018	340	420	1658	
% elongation @ break	336	300	326	413			266	205
Compression Set %								
23 C, 22 hours	33	13	17.8	41.8	26	36	20.3	36.20
70 C, 22 hours	51.2	51.2	61	54.5	40	60	63	81
Oil Swell % w/w								
23 C, 22 hrs	32	27	8	5	10	6	22	15
70 C, 22 hrs	66	58	34	19	52	31	35	28
% gel, xylene							81.42	72.28

\* Measured on compressed molded part

\*\* Measured on extruded part

The above examples show that use of branched polypropylene, preferably branched coupled impact polypropylene, results in TPVs with relatively higher  
5 hardness, higher tensile strength, lower elongation, higher resistance to oil, but also higher compression set. Coupled impact propylene copolymers should be used as matrix resin where a softer material with good compression set is desired.

The PP resins used in experiments 1-4 and in experiments 9-12 are considered high melt strength type (HMS). Using HMS polypropylene results in TPVs with  
10 relatively lower compression set, higher tensile strength, elongation, and higher strain hardening (higher stress at higher strains). The resistance to oil and processability (indicated by MFR) is somewhat better and extrudate surface quality is significantly better.

All EPDM used are of a relatively high ethylene level (70%) and medium ENB  
15 level. Keltan 5636A (available from DSM Copolymer Inc.) is a Ziegler-Natta catalyzed EPDM elastomer with a relatively broad molecular weight distribution ("MWD") and a medium ENB content. It has a Mooney viscosity of about 55 Mooney. Such EPDM produces TPVs with relatively lower hardness, higher melt flow rate, higher elongation than Nordel™ 3722IP (which is produced by a metallocene catalyst and has a relatively  
20 narrow MWD), with no significant differences in compression set or resistance to oil.

Increasing the ratio of EPDM/PP results in softer TPVs with relatively lower melt flow rates (i.e., processability), lower compression set, lower resistance to oil as well as tensile properties. The majority of commercial applications for TPVs require a hardness in the range of about 64 –73 Shore A. It is possible to make the compositions  
25 softer by increasing the amount of plasticizer, while maintaining the ratio of EPDM/PP as low as permitted to achieve desired tensile properties.

Increasing the amount of curing agent, such as SP1055, should increase the level of cross-linking, and should result in better tensile properties and resistance to oil. However, an excessive amount of uncured resin can react with itself, resulting in harder  
30 compounds, with undesired processing characteristics (lower MFR and higher gels). The optimum amount therefore depends on such other factors as mixing time, mixing

temperature and when zinc oxide is added. From this study, it appears that 7 parts of curing agent is the minimum required.

The function of accelerator is to speed up the curing reaction by reacting with free halide. Increasing the amount of the zinc oxide/curing agent ratio from 0.25 to 0.5  
5 had marginal or no effects on most properties; but the higher ratio proved to be beneficial to processability. It is also helpful that zinc oxide be dispersed well. In the above examples, free zinc oxide powder was used. Using masterbatch in polypropylene can produce better tensile properties. Preferably, it is more desirable to add zinc oxide after phenol is dispersed and curing has reached to a relatively high  
10 level.

The percentage of total elastomer cured was determined indirectly by extracting each formulation in boiling xylene. The amounts of polypropylene, oil, and stabilizers were subtracted from solution to determine the amount of rubber not cured (i.e., the soluble portion). The amount of rubber cured was determined by subtracting the  
15 amount of rubber not cured from the total.

As demonstrated above, embodiments of the invention provide a thermoplastic vulcanizate which has relatively increased tensile strength, elongation, compression set and/or oil resistance. Additional characteristics and advantages provided by embodiments of the invention are apparent to those skilled in the art.

20 While the invention has been described with reference to a limited number of embodiments, variations and modifications therefrom exist. For example, the thermoplastic vulcanizate need not be a mixture within the compositions given above. It can comprise any amount of components, so long as the properties desired in the thermoplastic vulcanizate are met. In some embodiments, the TPVs can comprise any  
25 other components not specifically described herein. However, in other embodiments, the TPVs may be substantially free of a component not described herein.

In another aspect of the invention, the TPV is made using a one step or two or more step compounding process, wherein the thermoplastic polymer is branched in conjunction with the production of the TPV. In one-step compounding using phenolic  
30 curatives, the compounding temperature preferably is maintained below 220°C to avoid breaking down the phenolic curative agent. In two-step compounding, the phenolic



curative agent is typically added during the second step and the temperature during the second step is maintained below 220<sup>0</sup>C.

Following are three brief exemplifications of processes for on-line branching of the thermoplastic polymer in combination with dynamic vulcanization:

- 5    Single-Step: Charge a mixture of 100 ppm - 450 ppm of DPO-BSA Concentrate Master Batch, polypropylene (homopolymer or copolymer (either random polymer or impact copolymer)), elastomer (such as EPDM), stabilizer, processing aid, ZnO and phenolic curative (such as SP1055) into a compounding extruder or into a mixer. Typical formulations to be used are described in Table 1 and 2. The extruder or mixer
- 10   should be operated so that the temperature profile within the zones of the extruder preferably does not exceed 220<sup>0</sup>C. Add oil or meter in oil slowly as the torque increases. Proper mixing screw needs to be employed to allow homogeneous mixing in case of the extruder approach. Finally the melt is cooled and pelletized.
- 15   Two-Step In An Extruder: In this aspect a screw compounding extruder with a high aspect ratio and having two feed hoppers is utilized. 100-450 ppm of DPO-BSA Master Batch is added with Polypropylene (homopolymer or copolymer (random or impact copolymer)) through the first feeder. The temperature in the first section is maintained between 200 - 250<sup>0</sup>C till the second feed hopper is reached. The
- 20   temperature in the extruder adjacent the second feed hopper is lowered to between 190C - 220<sup>0</sup>C. At the second feed hopper elastomer (such as EPDM), stabilizer, processing aid and phenolic curative (SP1055) is added. Subsequently oil is metered in. Typical formulations are described in Table 1 and 2. The final melt exiting the extruder is cooled and pelletized.
- 25   Two-Step In A Mixer: In a mixer (for example a Brabender batch mixer) charge PP (homopolymer or copolymer (random or impact copolymer) and 100-450 ppm of DPO-BSA and mix to a homogeneous melt at temperatures between 200C-250<sup>0</sup>C. Cool the mixture down to approximately to 190<sup>0</sup>C and add elastomer (such as EPDM), stabilizer
- 30   and processing aid. Mix for approximately 2 minutes and add phenolic curative. Add oil little at a time to

the formulation and as torque increases add ZnO and continue to mix for another 2 minutes. Typical formulations are described in Table 1 and 2. Finally cool the melt and granulate.

- 5 The TPV mixtures made using the one-step and two-step processes described above will have similar properties to those exemplified in the earlier examples.

The appended claims intend to cover all such variations and modifications as falling within the scope of embodiments of the invention.

What is claimed is:

1. A thermoplastic vulcanizate composition, comprising  
a mixture or reaction product of a branched thermoplastic polymer having a  
5 branching index of less than 1.0;  
a vulcanizable elastomer; and  
a cross-linking agent capable of vulcanizing the elastomer,  
wherein the cross-linking agent does not substantially degrade or cross-link the  
branched thermoplastic polymer.  
10
2. A method of making a thermoplastic vulcanizate composition, comprising:  
mixing a branched thermoplastic polymer having a branching index of less than  
1, a vulcanizable elastomer; and a cross-linking agent capable of vulcanizing the  
elastomer; and  
15 effecting vulcanization of the elastomer by the cross-linking agent;  
wherein the cross-linking agent does not substantially degrade or cross-link the  
branched thermoplastic polymer during vulcanization.
3. In claim 1 or 2, wherein the branched thermoplastic polymer is branched  
20 polypropylene having a weight average molecular weight,  $M_w^B$ .
4. In claim 3, wherein the branched polypropylene has a melt strength which is at least  
about 25% higher than that of a linear polypropylene having a weight average  
molecular weight substantially equal to  $M_w^B$ .  
25
5. In claim 4, wherein the melt strength of the branched polypropylene is at least about  
50% higher than that of the linear polypropylene.
6. In claim 4, wherein the melt strength of the branched polypropylene is at least about  
30 100% higher than that of the linear polypropylene.

7. In claim 4, wherein the melt strength of the branched polypropylene is at least 10 cN.
8. In claim 4, wherein the melt strength of the branched polypropylene is at least 15 cN.
9. In claim 4, wherein the melt strength of the branched polypropylene is at least 20 cN.
10. In claim 4, wherein the melt strength of the branched polypropylene is at least 25 cN.
11. In claim 4, wherein the melt strength of the branched polypropylene is at least 30 cN.
12. In claim 4, wherein the branched polypropylene is obtained by reacting a linear polypropylene with an azide compound.
13. In claim 3, wherein the branched polypropylene has a 1% secant modulus of greater than about 130,000 psi.
14. In claim 3, wherein the branched polypropylene has a 1% secant modulus of greater than about 150,000 psi.
15. In claim 3, wherein the branched polypropylene has a 1% secant modulus of greater than 170,000 psi.
16. In claim 1 or 2, wherein the branched polypropylene is a branched propylene homopolymer or copolymer.
17. In claim 1 or 2, wherein the branched thermoplastic polymer has a branching index of less than 0.8.

18. In claim 1 or 2, wherein the branched thermoplastic polymer has a branching index of less than 0.6.
- 5 19. In claim 1 or 2, wherein the branched thermoplastic polymer has a branching index of less than 0.5.
20. In claim 1 or 2, wherein the branched thermoplastic polymer has a branching index of about 0.2 to 0.8.
- 10 21. In claim 1 or 2, wherein the branched thermoplastic polymer is present in an amount from about 1% to about 99% by weight of the composition.
22. In claim 1 or 2, wherein the branched thermoplastic polymer is present in an  
15 amount from about 50% to about 99% by weight of the composition.
23. In claim 1 or 2, wherein the branched thermoplastic polymer is present in an amount from about 1% to about 50% by weight of the composition.
- 20 24. In claim 1 or 2, wherein the cross-linking agent is a phenolic resin.
25. In claim 1 or 2, wherein the cross-linking agent is present in an amount from about 1% to about 50% by weight of the composition.
- 25 26. In claim 1 or 2, wherein the cross-linking agent is present in an amount from about 5% to about 20% by weight of the composition.
27. In claim 1 or 2, wherein the cross-linking agent is present in an amount from about 1% to about 10% by weight of the composition.
- 30 28. In claim 1 or 2, wherein the elastomer is an ethylene-propylene-diene monomer (EPDM) copolymer.

29. In claim 1 or 2, wherein the elastomer is present in an amount from about 1% to 99% by weight of the composition.
- 5 30. In claim 1 or 2, wherein the elastomer is present in an amount from about 1% to 50% by weight of the composition.
31. In claim 1 or 2, wherein the elastomer is present in an amount from about 50% to 99% by weight of the composition.
- 10 32. In claim 1 or 2, wherein the composition is substantially free of a plastomer.
33. In claim 1 or 2, wherein the composition further comprises one or more additives selected from pigments, antioxidants, plasticizers, dyes, processing aids, stabilizers, or mixtures thereof.
- 15 34. In claim 1 or 2, wherein the elastomers constitutes the major phase and is present in an amount of at least 50% by volume of the composition.
- 20 35. In claim 1 or 2, wherein the elastomers constitutes the major phase and is present in an amount of at least 70% by volume of the composition.
36. In claim 1 or 2, wherein the branched thermoplastic polymer constitutes the major phase and is present in an amount of at least 50% by volume of the composition.
- 25 37. In claim 1 or 2, wherein the branched thermoplastic polymer constitutes the major phase and is present in an amount of at least 70% by volume of the composition.
38. In claim 1 or 2, wherein the branched thermoplastic polymer constitutes the continuous phase of the composition, and the elastomer is dispersed in the continuous phase.
- 30

39. In claim 2, wherein the vulcanization of the elastomer is effected by dynamic vulcanization.

40. In claim 2, wherein the mixing occurs simultaneously with the vulcanization of the elastomer.

41. In claim 2, wherein the mixing occurs prior to the vulcanization of the elastomer.

42. A thermoplastic vulcanizate composition, comprising  
a mixture or reaction product of

a branched polypropylene having a branching index of less than 1.0;  
an EPDM elastomer having ethylenic unsaturation; and  
a phenolic resin,

wherein the branched polypropylene has a weight average molecular weight in the range from about 100,000 to 1,000,000 and has a melt strength which is at least about 50% higher than that of a linear polypropylene having the same weight average molecular weight.

43. The composition of 42, wherein the composition is obtained by dynamic vulcanization.

44. The composition of 43 obtained by a dynamic vulcanization process, the process comprising:

(a) branching the polypropylene polymer by reacting with a coupling agent; and  
(b) vulcanizing the EPDM elastomer by reacting with a phenolic resin. .

45. The composition of Claim 44, wherein the dynamic vulcanization process is a one-step process.

46. The composition of Claim 44, wherein the dynamic vulcanization process is a two-step process.

47. The composition of Claim 44, wherein the coupling agent is a poly(sulfonyl azide).

48. A method of making a thermoplastic vulcanizate composition, comprising:

- 5       mixing a thermoplastic polymer, a vulcanizable elastomer, a coupling agent,  
      and a cross-linking agent capable of vulcanizing the elastomer; and  
      heating the mixture.

10   49. The method of Claim 48, wherein the cross-linking agent does not substantially  
     degrade or cross-link the branched thermoplastic polymer during vulcanization.

50. The method of Claim 48, wherein the method is a one-step process.

15

51. The method of Claim 48, wherein the method is a two-step process.

20   52. The method Claim 48, wherein the coupling agent is a poly(sulfonyl azide).

53. The method of Claim 48, wherein the coupling agent is a bis(sulfonyl azide).

25

54. The method of Claim 51, wherein the coupling agent is added during a first step  
and the cross-linking agent is added during a second step.

30   55. The method of Claim 54, wherein the mixing and heating are carried out in an  
     extruder.



56. The method of Claim 54, wherein the mixing and heating are carried out in a batch mixer.
- 5 57. The method of either of Claims 54 or 55, wherein the second step is carried out at a temperature of from about 190 to 220 C.
58. The method of Claim 54, wherein the first step is carried out at a temperature of  
10 from about 200 to 250 C.

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ning of each regular issue of the PCT Gazette.

(54) Title: THERMOPLASTIC VULCANIZATE COMPOSITION AND METHOD OF MAKING SAME

(57) Abstract: A thermoplastic vulcanizate composition comprises a mixture or reaction product of a branched thermoplastic polymer having a branching index of less than 1.0; a vulcanizable elastomer; and a cross-linking agent capable of vulcanizing the elastomer, wherein the cross-linking agent does not substantially degrade or cross-link the branched thermoplastic polymer. For example, a thermoplastic vulcanizate composition comprises a mixture or reaction product of a branched polypropylene having a branching index of less than 1.0; an EPDM elastomer having ethylenic unsaturation; and a phenolic resin, wherein the branched polypropylene has a molecular weight in the range from about 100,000 to 1,000,000 and has a melt strength which is at least about 50% higher than that of a linear polypropylene having the same molecular weight.

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## INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/16 C08L23/10

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## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 1 219 679 A (ADVANCED ELASTOMER SYSTEMS ;EXXONMOBIL CHEMICAL COMPANY IN (US)) 3 July 2002 (2002-07-03)  abstract; claims 1-20 page 3, line 3,35 page 4, line 53 page 5, line 5 page 6, line 13 page 8, line 12-48 page 9; table 1 page 13; table 3  --- -/--	1-11, 16-18, 20,21, 23-35, 39,40, 42,43,45

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

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## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-47

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-47

A thermoplastic vulcanizate and a method for making one (dynamically vulcanisation), comprising a branched thermoplastic polymer having a branching index of less than 1, a vulcanizable elastomer and a crosslinking agent, and effecting vulcanization of the elastomer wherein the crosslinking agent does not degrade or crosslink the branched thermoplastic polymer.

2. Claims: 48-58

A method for making a thermoplastic vulcanizate comprising mixing a branched thermoplastic polymer, a vulcanizable elastomer, a coupling agent, and a crosslinking agent, and heating the mixture.

## INTERNATIONAL SEARCH REPORT

 Inter      II Application No  
 PCT/US 03/08943

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 277 916 B1 (HO THOI H ET AL) 21 August 2001 (2001-08-21) abstract; claims 1-24 column 2, line 13-24 column 13, line 65 column 17, line 35 column 18, line 1-57 column 19, line 40 column 20, line 1-16 ---	1-47
X	EP 0 794 226 A (MITSUI PETROCHEMICAL IND) 10 September 1997 (1997-09-10) --- abstract; claims 1-9 page 3, line 40,54 page 4, line 25,55 page 5, line 45 page 6, line 1-47 page 7, line 10 page 8, line 15,45 page 10; table 1 ---	1-21,23, 25, 27-29, 31-35, 38,39, 41-45
A	US 2002 013 440 A1 (AGARWAL PAWAN KUMAR ET AL) 31 January 2002 (2002-01-31) abstract; claims 1-20 ---	1-47
A	WO 00 78858 A (ANSEMS PATRICIA ;DOW CHEMICAL CO (US); SILVIS H CRAIG (US); MADENJ) 28 December 2000 (2000-12-28) cited in the application abstract; claims 1-38 -----	1-47

## INTERNATIONAL SEARCH REPORT

 Interr I Application No  
 PCT/US 03/08943

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1219679 A	03-07-2002	US 2002128390 A JP 2002220493 A	12-09-2002 09-08-2002
US 6277916 B	21-08-2001	AU 3608600 A BR 0010275 A CA 2364438 A CN 1362977 T EP 1157066 A JP 2002538256 A WO 0052091 A	21-09-2000 15-01-2002 08-09-2000 07-08-2002 28-11-2001 12-11-2002 08-09-2000
EP 0794226 A	10-09-1997	AU 705660 B AU 1506297 A CA 2198998 A,C CN 1441000 A CN 1164544 A,B DE 69700305 D DE 69700305 T ES 2135274 T JP 9296063 A KR 216649 B TW 464672 B US 5786403 A	27-05-1999 11-09-1997 04-09-1997 10-09-2003 12-11-1997 12-08-1999 09-12-1999 16-10-1999 18-11-1997 01-09-1999 21-11-2001 28-07-1998
US 2002013440 A	31-01-2002	US 2001007896 A BR 0016286 A CA 2393598 A CN 1409731 T EP 1237963 A JP 2003516441 T WO 0142323 A US 2001053837 A	12-07-2001 27-08-2002 14-06-2001 09-04-2003 11-09-2002 13-05-2003 14-06-2001 20-12-2001
WO 0078858 A	28-12-2000	AU 5634300 A AU 5884000 A BR 0012197 A CA 2377008 A CA 2377655 A EP 1198512 A EP 1263873 A JP 2003518521 T WO 0078861 A US 2002156193 A US 2003092840 A US 6472473 B	09-01-2001 09-01-2001 12-03-2002 28-12-2000 28-12-2000 24-04-2002 11-12-2002 10-06-2003 28-12-2000 24-10-2002 15-05-2003 29-10-2002